

## Spectroscopy of a Eu(III)-imidazolate complex

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### Abstract

We have performed semi-empirical calculations on a Eu(III)-imidazole complex. We use a Scaled Quantum Mechanical Force field approach from the MOPAC software. We obtain molecular force constants used in the normal mode calculation to modelize experimental Raman frequencies. Furthermore, we discuss the structure and the electronic properties of this complex by means of spectroscopic techniques such as photoluminescence and X-Ray Absorption Near-edge Spectroscopy (XANES).

**Keywords:** imidazole, semi-empirical calculations, Raman spectroscopy, photoluminescence, X-ray absorption spectroscopy.

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### 1. Introduction

The imidazole molecule ImH is a planar heteroaromatic pentacyclic ring of considerable interest owing to its presence in biological systems of a complex nature such as histidine residues and globin. This molecule can be deprotonated in a strong basic medium to give the imidazolate anionic form Im<sup>−</sup> which easily bounds to metal ions. Final products are imidazolate complexes which have been widely investigated, especially with transition metal ions [1]. These compounds provide interesting perspectives for technological applications like biosensors, luminescent tracers, catalysts, complexation of toxic metals for environmental chemistry, and chemical waste treatment.

This work is intended as a thorough investigation of the vibrational properties of a Eu(III)-imidazolate complex in order to assign Raman spectral bands, for which references in the chemical literature are lacking. Our approach makes use of the MOPAC software. Secondly, an almost complete determination of the structure of our complex has been achieved with X-Ray Absorption Near-Edge Spectroscopy (XANES). Finally, fluorescence spectra have been recorded and show unambiguously charge transfer between the host matrix and the rare-earth metal ions in the complex [2].

### 2. Experimental

Reagent imidazole was purchased from Aldrich and Co. The Eu(III)-imidazolate amorphous complex was subsequently prepared by the route of Bauman and Wang [3]. Raman spectra were recorded on a multichannel Jobin-

Yvon T64000 spectrometer and a FT-Raman spectrometer. XANES spectra were recorded at LURE (Orsay, France) using X-ray synchrotron radiation emitted by the DCI storage ring (1.85 GeV positrons, average intensity of 250 mA). Data were collected in the transmission mode at the Eu L2 and L3 edges on XAS4 spectrometer, using a double crystal monochromator Si(311). Harmonics were rejected by mirrors with a cut off at 12 keV. The imidazolate-complex fluorescence was recorded on a 1680 Spex spectrofluorometer at room temperature and detected with a Peltier-cooled photomultiplier tube. The set-up allowed to obtain both excitation and emission spectra. The excitation source was a 450 W Xe lamp.

### 3. Results and discussion

#### 3.1. Raman spectroscopy and semi-empirical calculations

Calculations of the imidazolate anion were carried out by the complementary use of the semi-empirical MOPAC software and the Scaled Quantum Force Field (SQF) method to obtain scaled force constants and vibrational frequencies. In this technique the number of adjustable scaling factors does not exceed the number of normal frequencies, and we consider only the in-plane vibrations. The first step was to calculate the equilibrium geometry of Im<sup>−</sup> with the PM3 Hamiltonian in MOPAC. Subsequent application of the SQF technique has allowed to obtain scaled normal frequencies giving an optimal correspondence with the experimental Raman ones. The results are summarized in Table 1. Spectra taken from the europium complex with visible light excitations are dominated by a line at 1065 cm<sup>−1</sup> corresponding to the totally symmetric bending vibration of the C-H bonds (Fig. 1, top). In our calculations this line is the most prominent mode, while other bands are more than 5 times

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weaker. We assume that the  $1065\text{ cm}^{-1}$  line enhancement upon visible light excitation, which does not occur in UV-Raman spectra, is a resonant excitation of totally-symmetric modes due to a charge transfer from the Im<sup>-</sup> anion to the metal cations. This charge transfer excitation is strongly coupled to the Raman-active modes. The other calculated frequencies for other rare-earth and transition metals complexes also match the Raman spectra well, except for the  $854\text{ cm}^{-1}$  line for which two calculated bands are obtained at  $846$  and  $866\text{ cm}^{-1}$ . Such a discrepancy may arise from the fact that the free-molecule approximation is no longer valid below  $900\text{ cm}^{-1}$  where strong admixture of internal and external modes is likely to occur.

### 3.2. XANES

The XANES spectrum of the Eu(III)-imidazolate complex has been compared to that of a standard ( $\text{Eu}_2\text{O}_3$ ) in which europium ions are in an octahedral environment and in a defined 3+ oxidation state. There is evidence that the standard compound and the imidazolate complex have the same absorption edge at an energy of  $7628\text{ eV}$ . Moreover, none of them presents a pre-peak edge, which is evidence for an identical symmetric environment in the two materials. We therefore expect that the europium cations in the complex are octahedrally coordinated with a 3+ oxidation state. These conclusions are confirmed by the Mössbauer spectrum recorded at  $77\text{ K}$  which shows isomer shift and quadrupolar splitting with values that are actually characteristic of the above features.

### 3.3. Photoluminescence

We have recorded fluorescence spectra of our complex at different excitation wavelengths (Fig.1, bottom). They are composed of bands with maxima at  $593$ ,  $616$  and  $696\text{ nm}$ . These emissions are clearly characteristic of the  $\text{Eu}^{3+}$  ion [4]. However, the excitation spectrum of the  $616\text{ nm}$  transition ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) shows a contribution due to the imidazole matrix ( $\sim 250\text{ nm}$ ). Subtraction of the diffuse reflectance spectrum of imidazole from that of the europium imidazolate complex confirms this point, since a new absorption band appears at low wavelengths ( $\sim 250\text{ nm}$ ) not associated with a  $\text{Eu}^{3+}$  absorption. We believe this band comes from a charge transfer between the host matrix and europium ions. The experimental observation of such a

feature agrees well with theoretical calculations on vibrational spectra. The different vibrational behaviour of europium imidazolate and pure imidazole may therefore be explained by this charge-transfer process.

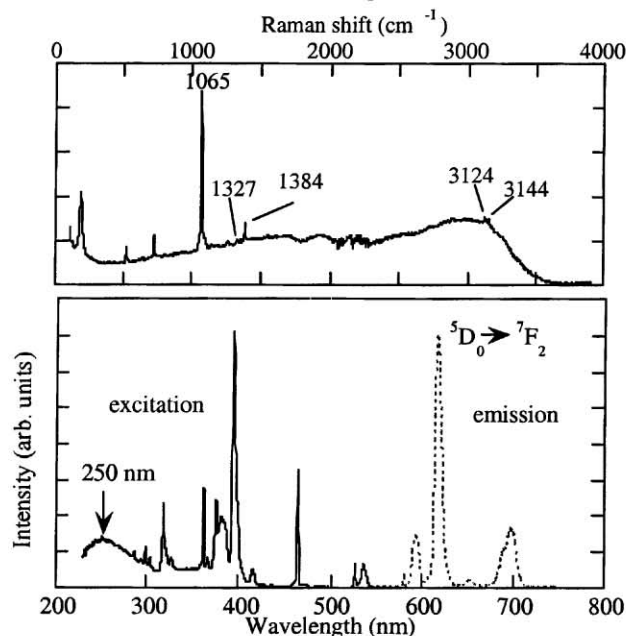


Fig. 1. Excitation, emission and Raman spectra of Eu:imidazolate

### 4. Conclusion

In this work, we have presented a spectroscopic study of a Eu(III)-imidazolate complex. We have obtained a complete vibrational assignment for the imidazolate anion. We have shown that a charge transfer excitation is likely to occur in the complex. Additionally, the structure of the complex as concerns metal ion environment and oxidation state has been partly deciphered by means of XANES and Mössbauer spectroscopy.

### References

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Table 1: Optimized geometry, experimental and calculated Raman frequencies of the imidazolate anion with assignments and relative intensities.

		Optimized geometry (cartesian coordinates)		Frequencies ( $\text{cm}^{-1}$ )		Relative int. (%)	Assignments
		X	Y	Exp.	Calc.		
	H1	-2.2366	0.0000	854	846	4.3	Ring def.
	C2	-1.1495	0.0000		866	0*	Ring def.
	N3	-0.3688	1.1296	971	971	0	Ring def.
	N4	0.3688	-1.1296	1065	1069	100	Symm. bend. H7-C5/H8-C6
	C5	0.9494	0.6981	1100	1095	0	Ring rotation
	C6	0.9494	-0.6981	1328	1327	18.7	Symm. stretch N3-C5/N4-C6
	H7	1.7795	1.3964	1384	1388	0	Antisymm. stretch (C2-N3)-(N3-C5)/
	H8	1.7795	-1.3964	1451	1450	19	Ring def.] (C2-N4)-(N4-C6)
				1628	1628	12.8	Stretch C5-C6
				3124	3123	0	Stretch C2-H1
				3124	3126	0	Stretch C5-H7/C6-H8 out-of-phase
				3144	3144	0.4	Stretch C5-H7/C6-H8 in-phase

\* The calculated intensities are 0 for anti-symmetric vibrations. The Raman bands observed for Eu(III)-imidazolate are listed in italics.